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## Note

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# Response of a filter-less flame photometric detector to hetero-organics

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Since its wedding with gas chromatography by Brody and Chaney[1], flame photometry of $S_2$ and POH species has been widely used for analytical purposes, especially in the areas of pesticide and petroleum chemistries. Although the emission phenomenon is far from being completely understood[2], its analytical usefulness is undisputed (*e.g.* ref. 3).

The Brody–Chaney detector and commercially available versions thereof, owe much of their impressive performance to the cup surrounding the flame and shielding it from direct view of the photomultiplier tube. It is commonly assumed, however, that the selectivity of phosphorus or sulfur against carbon compounds is due, at least in part, to narrow-bandpass interference filters (at 526 and 394 nm, respectively). It was therefore interesting for us to investigate how much the filters actually contributed to this purpose, and what characteristics the flame photometric detector (FPD) would display without a filter.

As a second point of interest, we wanted to explore the remote possibility of increasing the signal for phosphorus and especially sulfur compounds, by dispensing with the filter. Although this approach may seem unconventional, it should be remembered that the band spectra of POH and $S_2$ cover a more extensive wavelength region than the filters. Operating the FPD without a filter, of course, went far beyond these regions to the spectral limits of the photomultiplier. The question apparent was which other species would respond within these limits.

Therefore, as a third point of interest, we decided to measure the response of hetero-organics other than those of phosphorus and sulfur. It had been reported that boron[4] and chromium[5] yield FPD responses; and our own experience with a shielded, hydrogen-rich flame[6] also seemed to encourage that interest.

## EXPERIMENTAL

A commercial FPD (Tracor, Austin, Texas, U.S.A.) was used on a gas chromatograph manufactured by the same firm. In one-channel operation, the interference filter was replaced by a rectangular opening cut into a thin disc of blackened alumi-

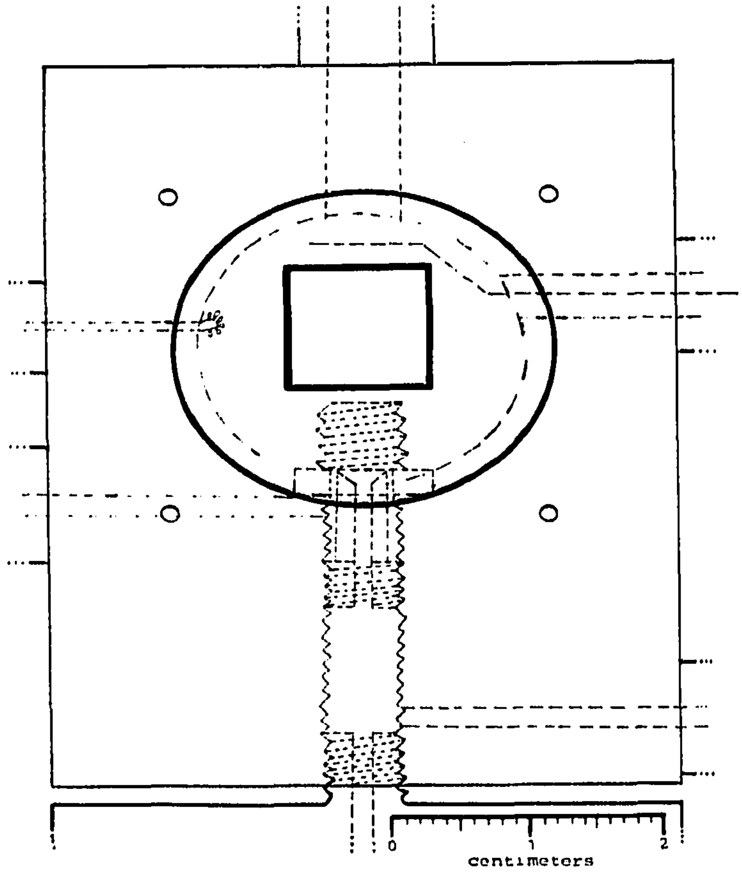

Fig. 1. Dimensions and position of aperture.

num. Fig. 1 shows this aperture in strong lines. Other detector parts are indicated schematically by weak lines to define the relative position of the aperture (The cup surrounding the flame differs somewhat from the original, commercial one; but this change should be incidental in the context of this study).

Various hetero-organics were chromatographed on 3% OV-101 on Carbowax 20M-modified Celite 545 (ref. 7) contained in a 1.5 m×2 mm I.D. borosilicate glass column. The flow-rates in ml/min were: $H_2$, 140; $O_2$, 27; Air, 60; $N_2$, 15; and the detector base temperature was kept at 240°. The column temperature was adjusted such that the compounds eluted with retention times between 1.2 and 2.5 min.

## RESULTS AND DISCUSSION

Fig. 2 gives an overview of the results obtained. Darkened symbols denote measurements through 393 or 525 nm interference filters, empty symbols indicate their absence. The graph, otherwise, is self-explanatory and it reflects conventional calibration curves—except for the use of signal-to-noise ratios as the ordinate.

This use is necessary for a meaningful analytical comparison: As expected, the

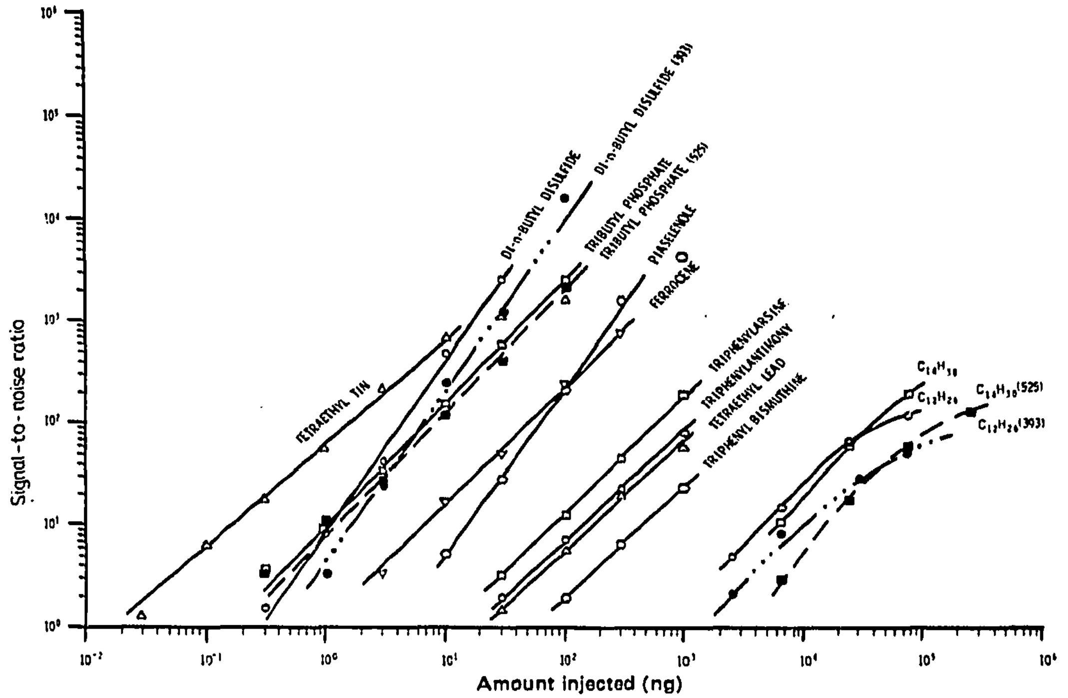

Fig. 2. Relationships between signal-to-noise ratios and amounts injected for various compounds. For details, see text.

signals for $S_2$ and POH increased considerably when the filter was removed—but so did, to some degree, the noise level. The net gain was apparent but small.

Surprisingly, the loss in selectivity of phosphorus and sulfur *vs. n*-hydrocarbon model compounds was also comparably small: Selectivity against carbon, at least in this particular case, did not significantly depend on the presence of a filter. The filters thus play a major role only in distinguishing P from S compounds; and, in the case of, say thiophosphates, in providing a linear calibration curve at 526 nm.

The calibration curves of Fig. 2, with the exception of those for sulfur and selenium compounds, are essentially linear, *i.e.* they show a 45° slope. Perhaps it should be emphasized at this point that the response of the test compounds is by no means defined according to source, and only spectral scans could provide information on its origin. It is well known, for instance, that aromatic structures have higher luminosities than aliphatic ones; and several other effects could have influenced the observed signals.

In the stronger-responding compounds, however, the hetero-atom is the one most likely involved in the emission process. Truly outstanding is the case of tetraethyltin with a minimum detectable amount of 30 pg; a rather welcome finding in view of the many disparate applications tin compounds find in industry and contemporary life[8]. Tetraethyltin can be determined with equal sensitivity through hydrogen-rich flame ionization[9], or, less sensitive, through air-rich flame photometry[10], but neither of these possibilities could be conveniently realized with the commercially available FPDs.

Further studies are definitely needed to confirm the suspected sources of radiations observed. From an analytical viewpoint, such flame photometry with shielded flame, but without filter, may have potential as a scanning technique for a variety of hetero-atoms. It is quite sensitive—*e.g.* thiophosphates should show up stronger without than with either phosphorus or sulfur filter—and the discrimination against aliphatic carbon does not seem significantly impaired. It is quite probable that heteroatoms other than the ones tested, would yield equally interesting results.

## ACKNOWLEDGEMENT

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